Functionalized Surfaces
(62234N)

Goal:

To cleanup solutions

by synthesizing novel

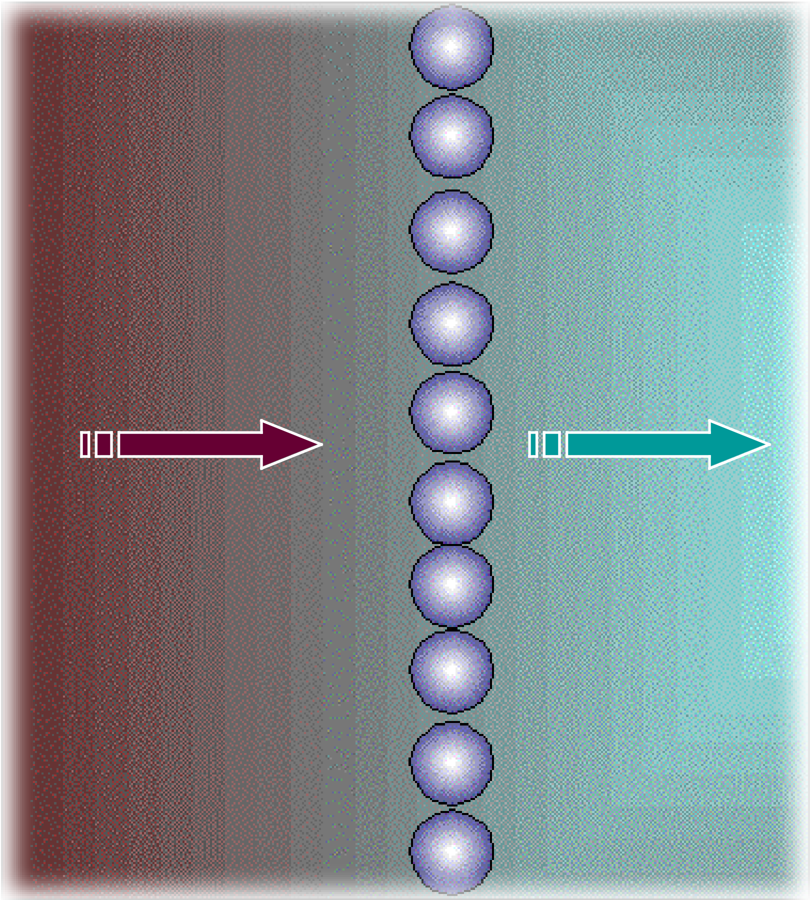
chelating materials

That can remove heavy

metal ions from feed

streams.

6.2 Review
August 2, 2001



Functionalized Surfaces

Payoff:

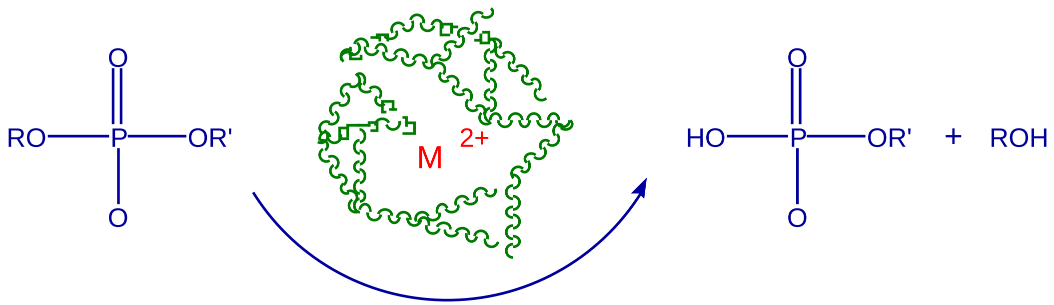
To enable the USN to access environmentally sensitive bodies of water worldwide. Additional benefit using same approach to make reactive surfaces for management of pesticides used by DoD.

Breakout into 2 major task areas:

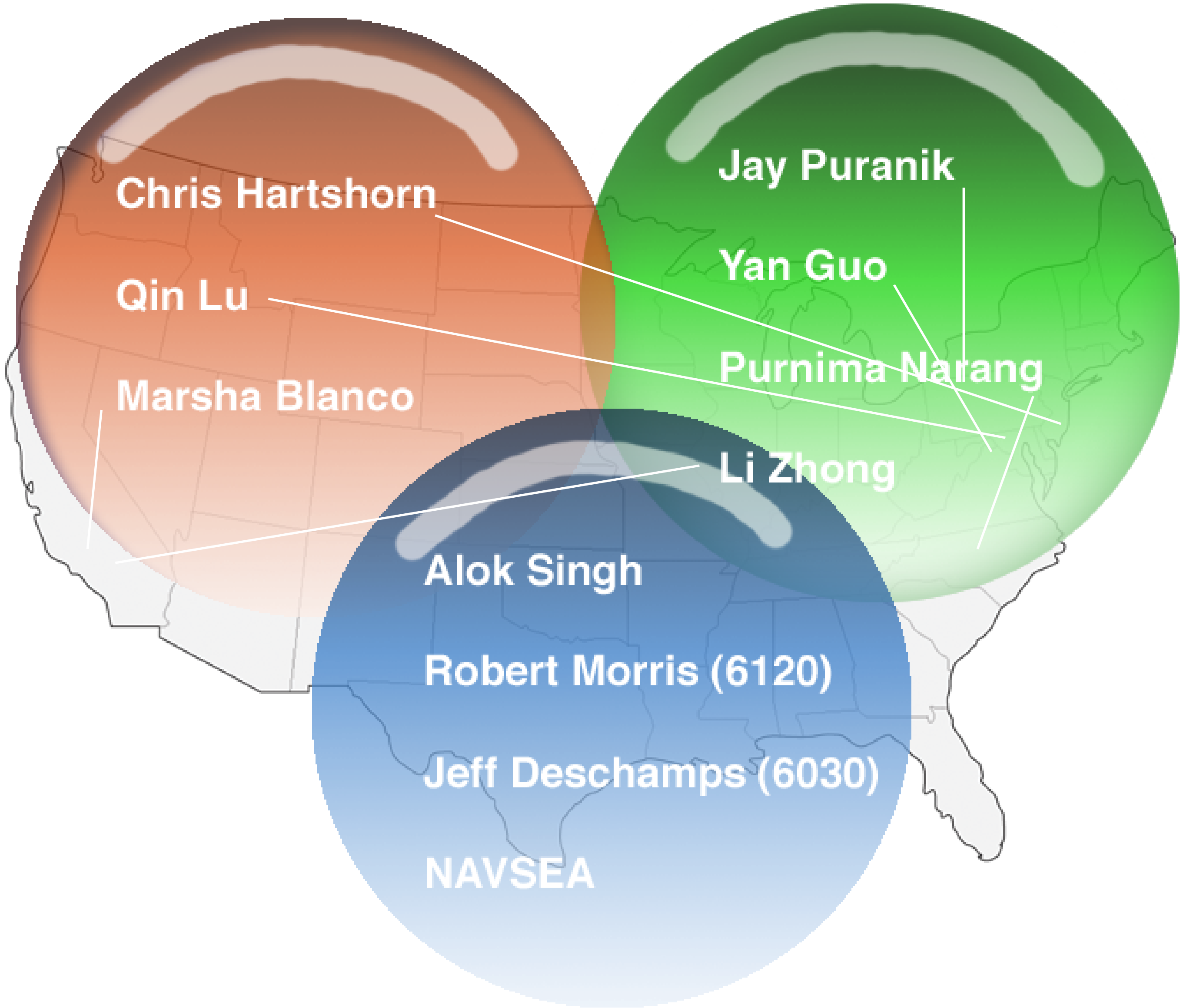
-*Chelation Surfaces Transition- Facilitation*

and

-*Catalytic Properties of Chelating Polymers*.



Contributors



Environmental Standards for Heavy Metals

How Clean?

-Drinking water standards:

- **Cu 0.001 ppm**
- **Pb 0.015 ppm**
- **Hg 0.002 ppm**

-Receiving water standards:

- **< whatever it happens to be.**

-Navy Jet Fuel

- **Cu 0.010 ppb**

Present Picture

DoD-Related Problems with Heavy Metals

- Small arms ranges
- Underwater hull maintenance
- Aircraft wash racks
-Bilge water
-Cu in jet fuel (non-environmental)

Present Solutions

-Neutralization/precipitation (50 ppm)

-Capping/vitrification (n.a.)

--Electrolytic recovery (50 ppm)

-Ion exchange/adsorption (1 ppm)

Issues for Jet Fuel Copper Removal

The Impact of Dissolved Copper in JP-5

- The majority of fuels will be degraded with as little as 10 – 15 ppb copper

- Dissolved copper can induce chemical changes in jet fuel
    - catalyzes thermal oxidation in hot sections of jet engine
    - induces deleterious chemical changes in ambient storage
        - greatly accelerates engine nozzle coking
        - Increases maintenance frequency

- Estimated $10M / year cost of nozzle replacement

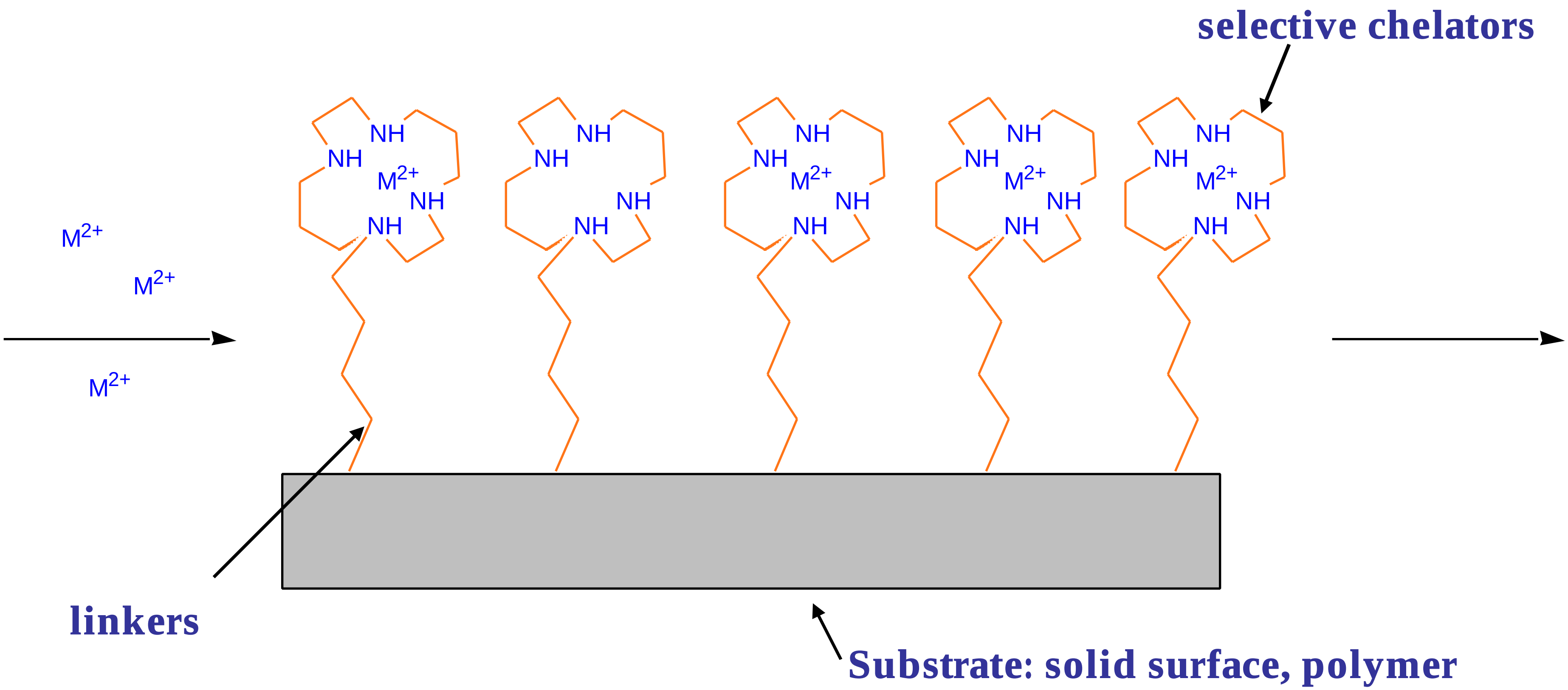
Strategies for Dealing with Dissolved Copper in JP-5

- addition of soluble copper chelant (metal deactivating additives)
    - soluble copper complex is thermally unstable – liberates copper in hot sections
    - thermal stability test (JFTOT) issues with metal deactivator additives

Scenario

Immobilization on Solid Surface

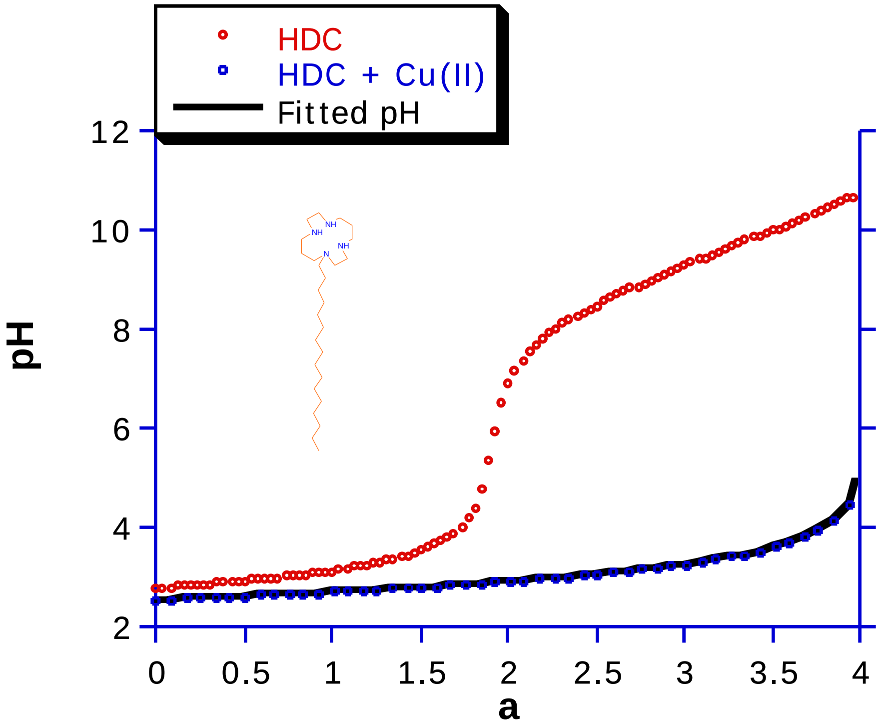
(Jay Puranik, Yan Guo, Purnima Narang)

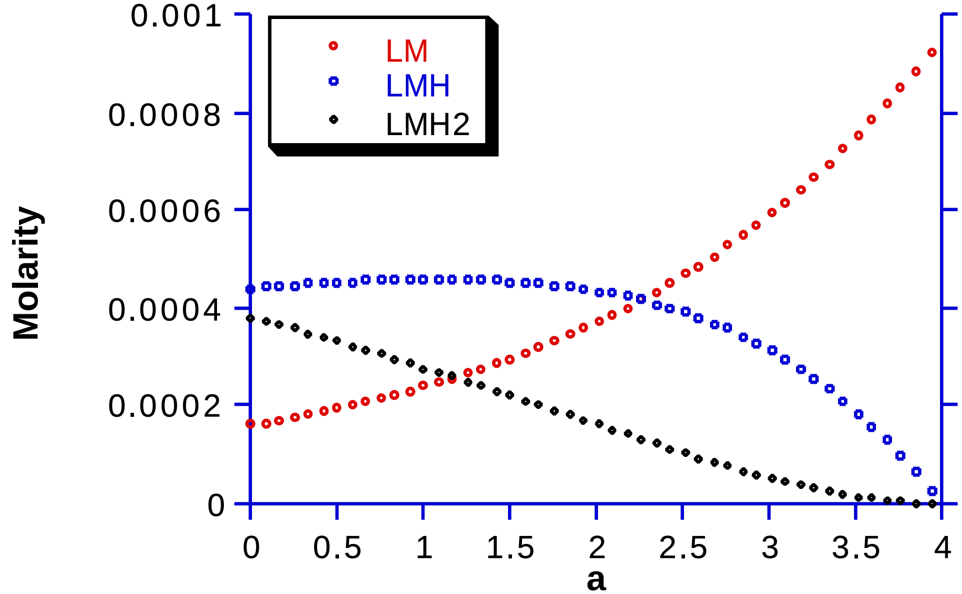


Getting Stability Constants and Species

Titration Curves

Most Prevalent Species





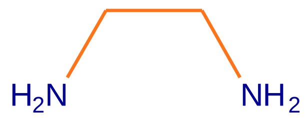
(Log K_{cu} = 20)

Chelators

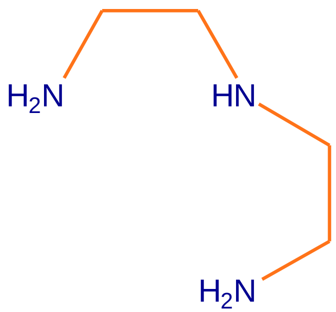
Cyclic
(1st generation)

Hexadecylcyclam
(HDC)
Log K_{cu} = 20

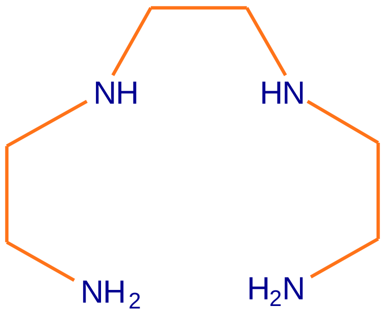
Acyclic
(2nd generation)



ethylenediamine
(EDA)

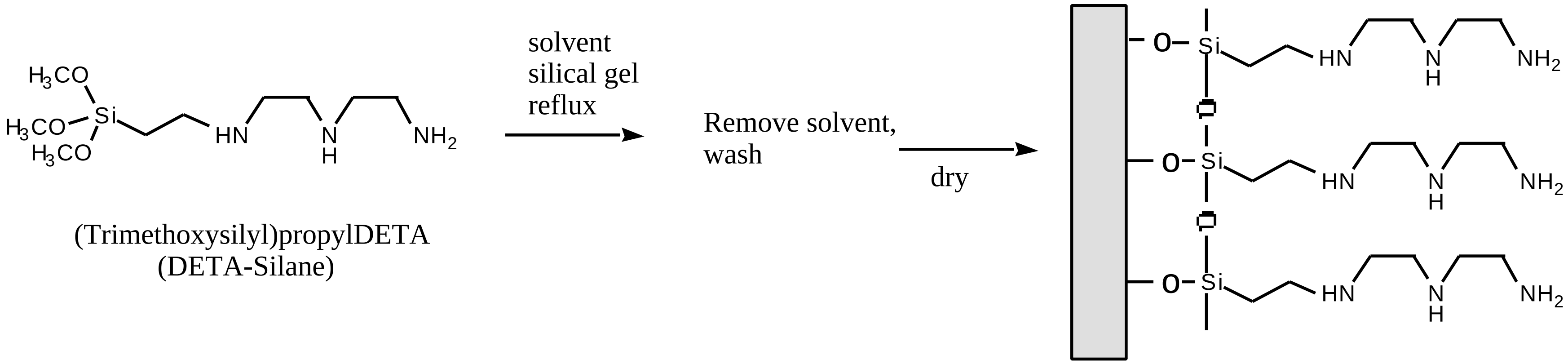


diethylenetriamine
(DETA)
Log K_{cu} = 16



triethylenetetramine
(TETA)
Log K_{cu} = 20

General Procedure for Immobilizing DETA-Silane to Silica Gel



(Trimethoxysilyl)propylDETA
(DETA-Silane)

Parameters for optimization of procedure:

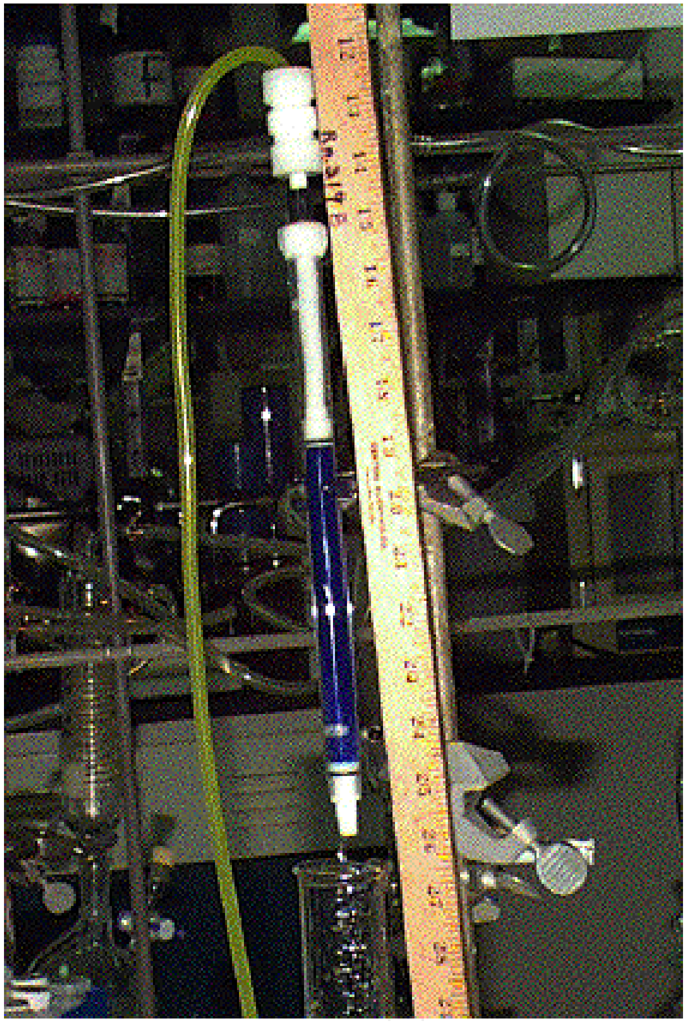
- Silica gel mesh-size: 20-60, 70-230,... (70-230 best)
- Ratio of silane to silica: from 1:8 to 2: 1 (1:1)
- Pre-treatment of silica: dry or not, acid wash or not? (no pretreatment ok)
- Solvent choice: toluene, methylene chloride, etc (toluene)
- Water as catalyst: add water or use naturally adsorbed water? (Don't add water)
- Annealing:
  - sequence of washing and baking? (Either ok)
  - Temperature? (dry between 60 - 80 °C)
  - Time? (24 h)

Comparison of Modified Silica Capacities (static)

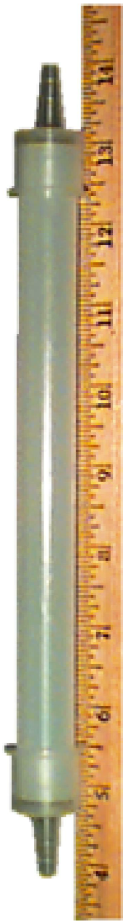
Chelator	Mesh	Max. Capacity (mg Cu/g silica)
Aminopropyl*	230-400	52
Ethylenediamine*	230-400	17
DETA	70-230	51
DETA	30-60	12
Plain Silica	70-230	3

*Commercially obtained samples.
Aminopropyl capacity is excellent, but mesh size is too fine for high volume flow applications.

Lab-Scale Test Columns

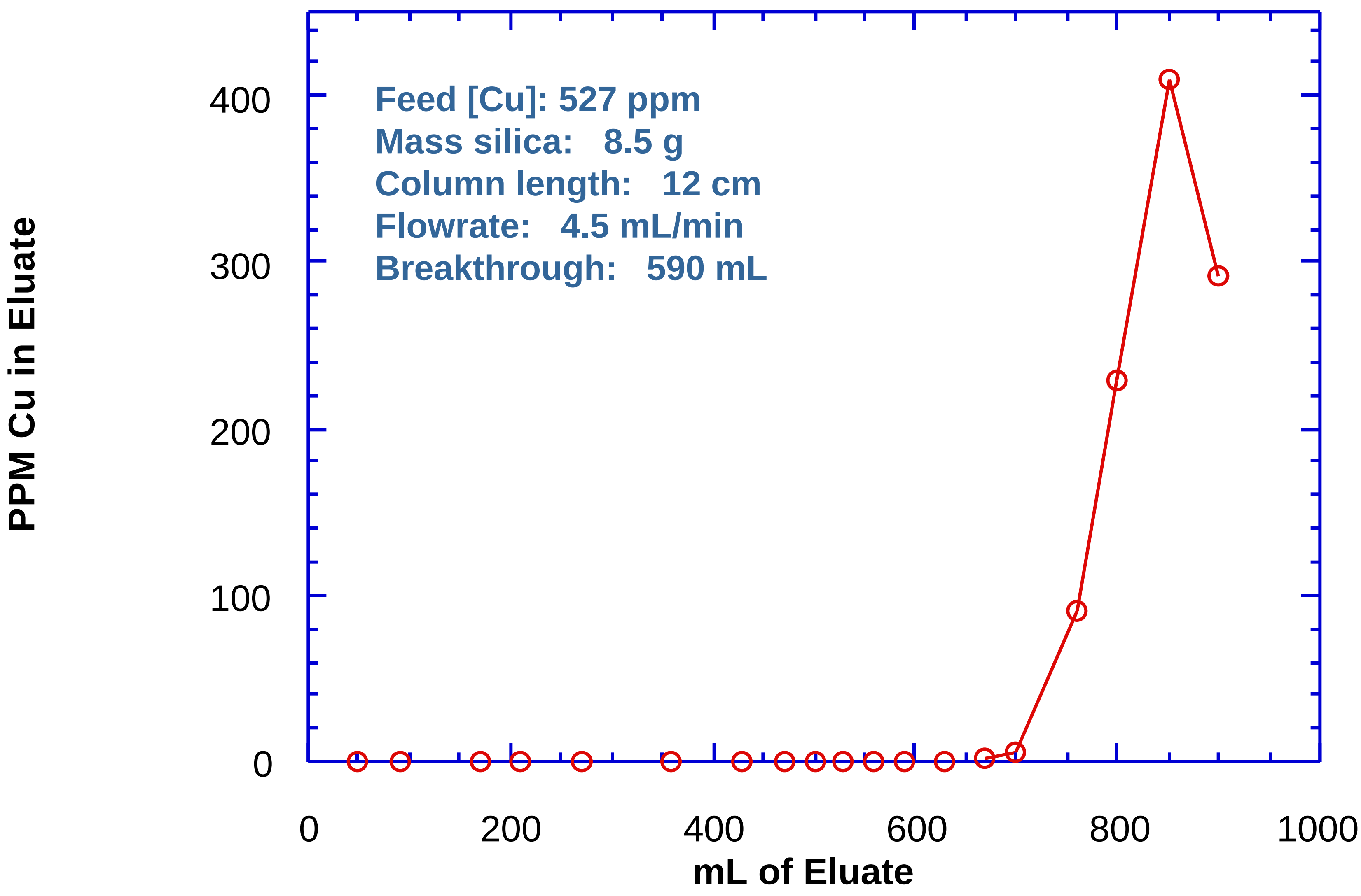


DETA-silica glass column with copper feed



Plastic tubes for jet fuel

Column Elution Profile for DETA-Silane (70-230)



Cost-Estimates/Technical Issues

Acyclic Polyamine Chelants (DETA)

- estimated material cost ~ \$0.09 / g modified silica
- copper capacity ~ 36 mg Cu / g modified silica
- able to remove copper from Cu-MDA in fuel
- projected cost of ~ \$0.01 / gallon jet fuel containing 1000 ppb Cu

Technical Issues

- verification that DETA-Si exposure removes only copper
- backpressure / flowrate optimization
- solid support particle size, filter medium volume
- filter housing design
- capacity indicator design

Scale-Up / Field Testing

- CRDA with Pall Aeropower and NAVSEA for scale up engineering
- Scale-up to 600 gpm (eventually)

Pall, NAVAIR, NRL CRADA

- Joint CRADA with NAVSEA to develop and test technology for jet fuel copper-removal.

- NRL: Supply and transfer materials and technology
Code 6930 and Code 6120

- NAVSEA: Define testing standards and perform tests

- Pall: Design and supply filter housing for material

Currently Undergoing Tests

CRDA between Pall Aeropower Corporation, NAVAIR, and NRL.

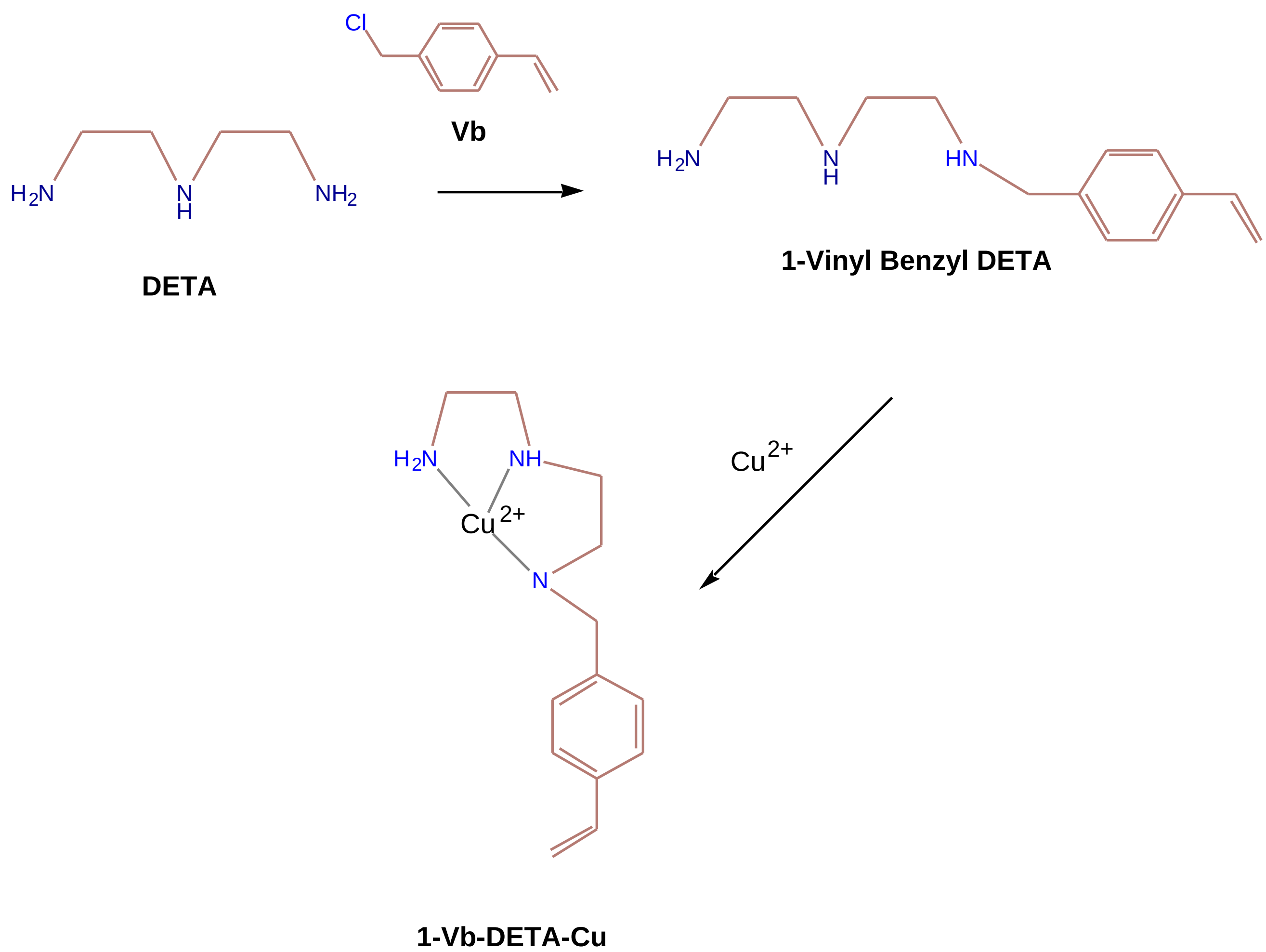
Test site at Pax River Naval Air Base

Polymer Approach

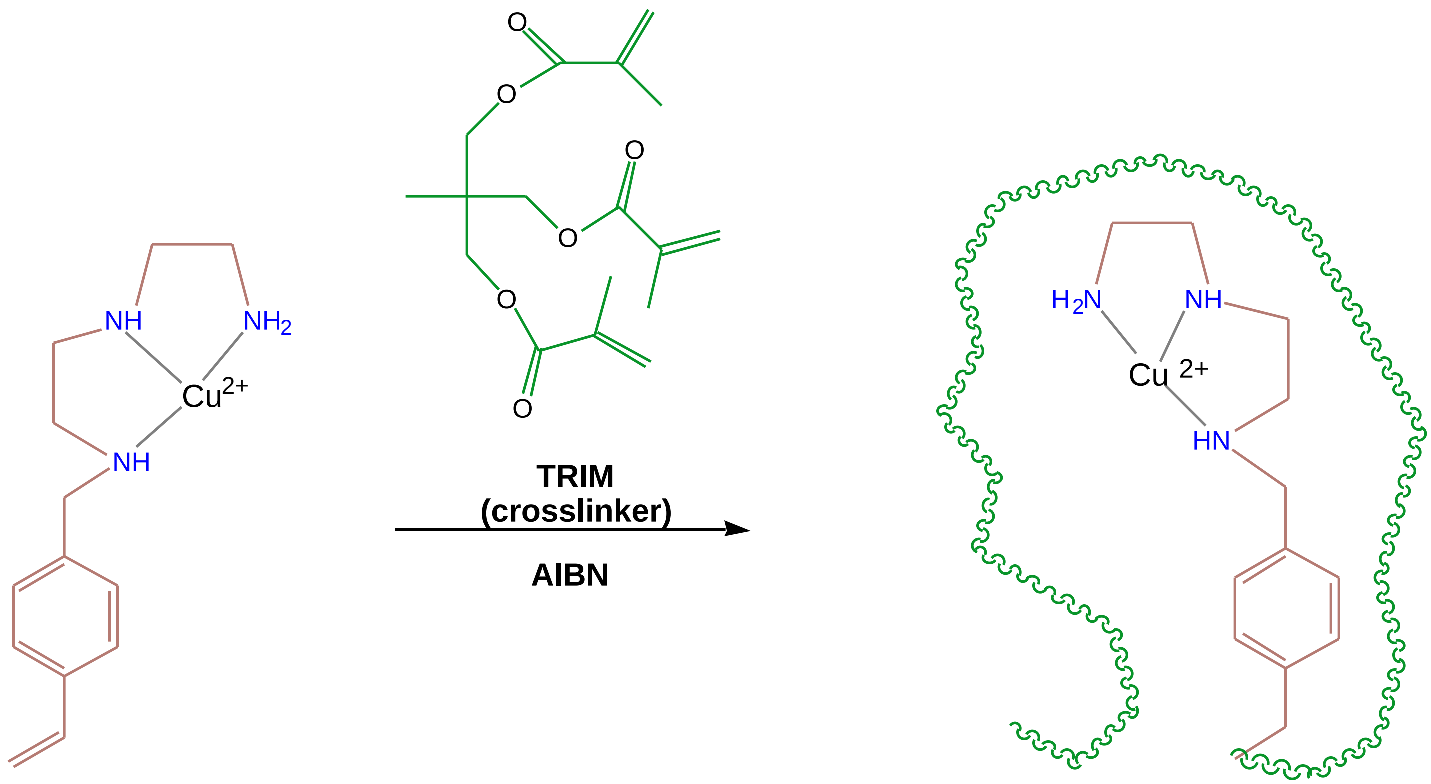
Alternate polymer approach for greater stability, variety of materials, and selectivity:

- **Pre-organize chelator-metal complex (pseudo macrocyclic)**
- **Lock-in pre-optimized coordination geometry**

Making Functional Monomers by Templating



Crosslinking to Lock in Conformation/Site



1-Vb-DETA-Cu

DVb Deta polymer

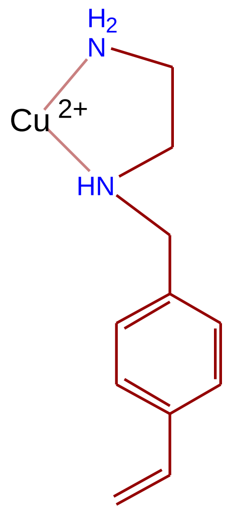
Advantages of Polymers over Solution Catalysis

- **Polymer form allows catalysis over a wider range of pH:**
  - **-No precipitation**
  - **-No changes in ligand-metal ratios**
- **Extremely stable.**
- **Easy separation of products from catalysts.**
- **Very cost-effective.**
- **Enhances efficiency over solution catalysis. (surprise)**

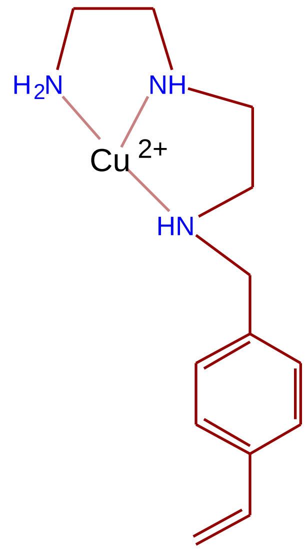
Anticipated Issues

- **Distortion of coordination geometry**
- **Hindrance of chelator motion**
- **Unfavorable presentation of substrate**
- **Unavailability of sites**
- **Diffusion limitations**

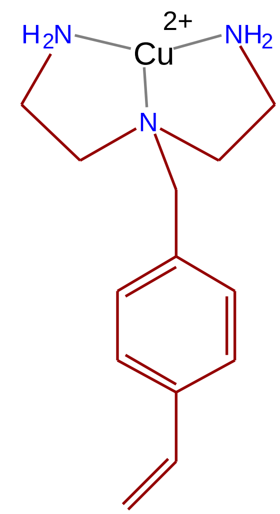
Chelator Complexes



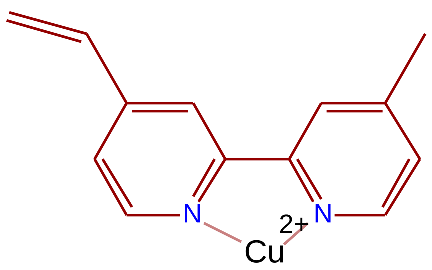
1-(4-vinyl)benzyl EDA



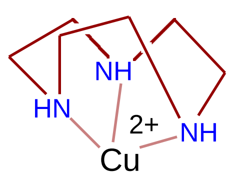
1-(4-vinyl)benzyl DETA



4-(4-vinyl)benzyl DETA

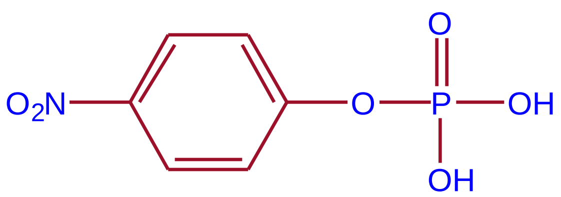


4-vinyl-4'-methyl-2,2'-Bipyridine: Cu(II)

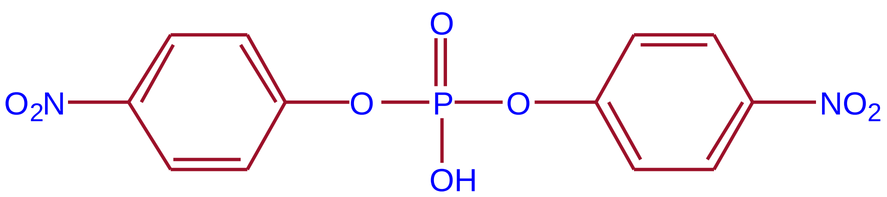


Cyclononane: Cu(II)

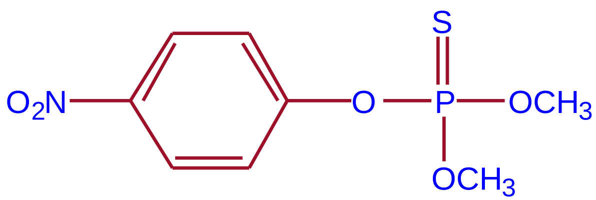
Substrates Studied



Nitrophenylphosphate
(NPP)



Bis-nitrophenylphosphate
(BNPP)

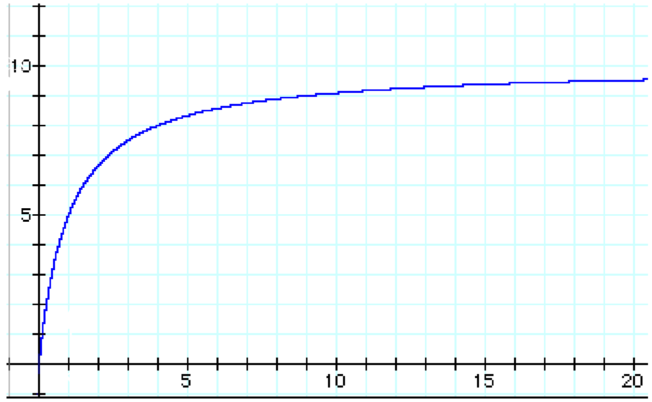


Methyl Parathion
(MeP)

Michaelis-Menten Model

$$S + C \underset{K_2}{\overset{K_1}{\rightleftharpoons}} X \xrightarrow{K_3} P + C$$

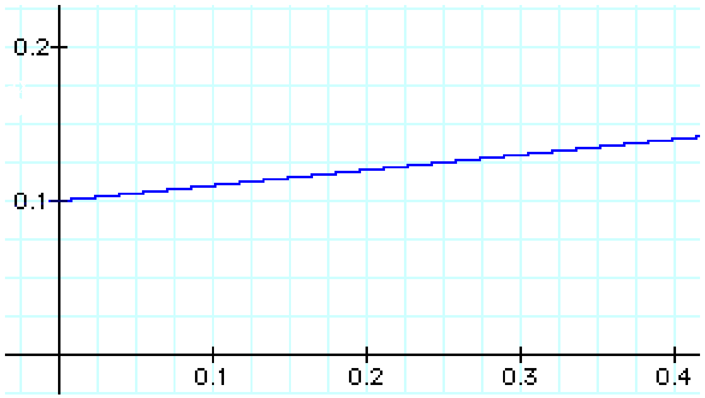
Reaction Rate: $$\frac{dP}{dt} = \frac{V_{max}}{K_m + S_o} S_o$$



Apparent rates: $$V_{max} = K_3 C_o$$

Lineweaver-Burk Linearization:

$$1/v = \frac{K_m}{V_{max}} 1/S_o + \frac{1}{V_{max}}$$



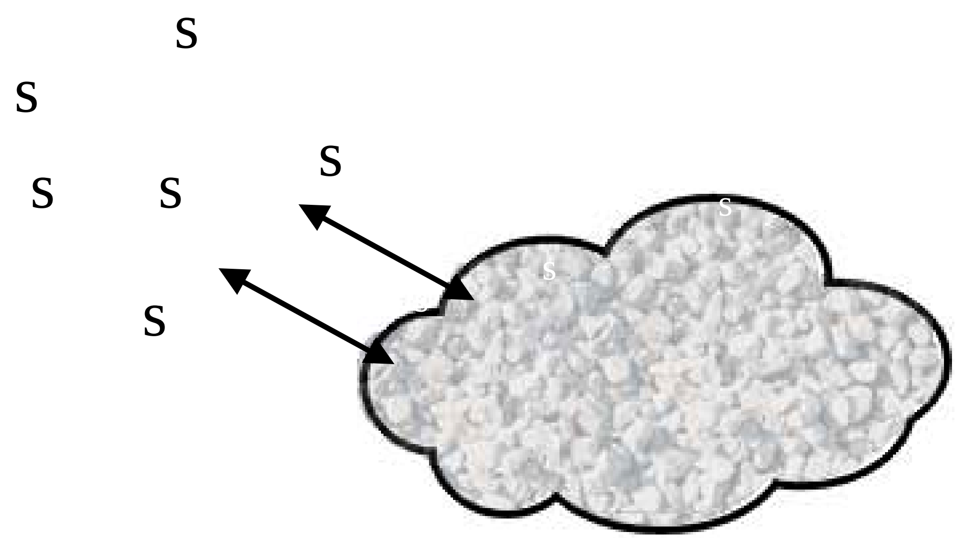
Polymer is an Active Partner

Binding capacity for range of substrate concentrations:

50 - 220 mg MeP/g polymer

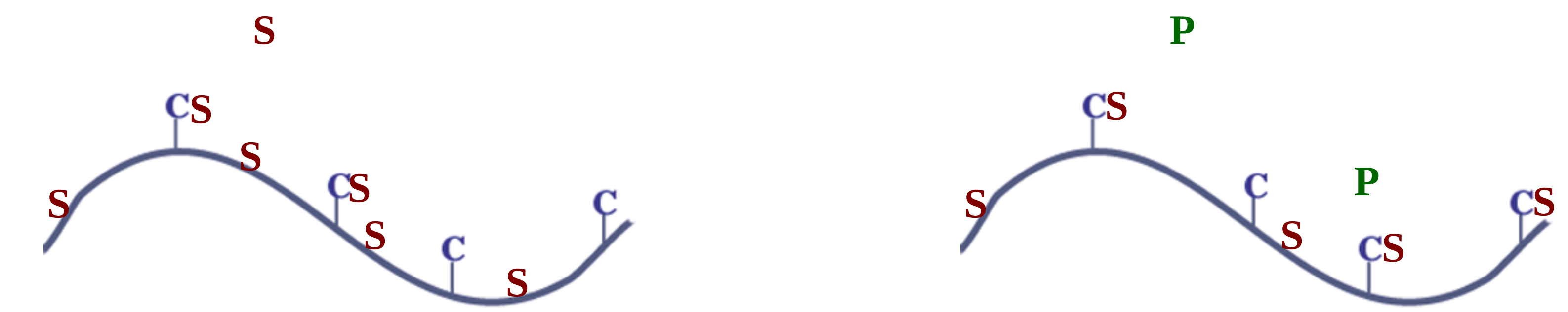
Vs.

0.01 - 0.05 mg MeP/g clays



Surface Picture

Substrate binds quickly to polymer.



Subsequent hydrolysis from bound pool.

Relationship of Heterogeneous Catalysis to Michaelis-Menten Model

Heterogeneous Model

$$A + S \underset{k_{-A}}{\overset{k_A}{\rightleftharpoons}} A{\bullet}S \xrightarrow{k_{cat}} P{\bullet}S \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} P + S$$

Assuming catalytic step is rate-limiting:

$$\frac{dP}{dt} = \frac{k_{cat}(1/K_A)C_A C_{cat}}{1 + \dfrac{C_A}{K_A} + C_P K_P}$$

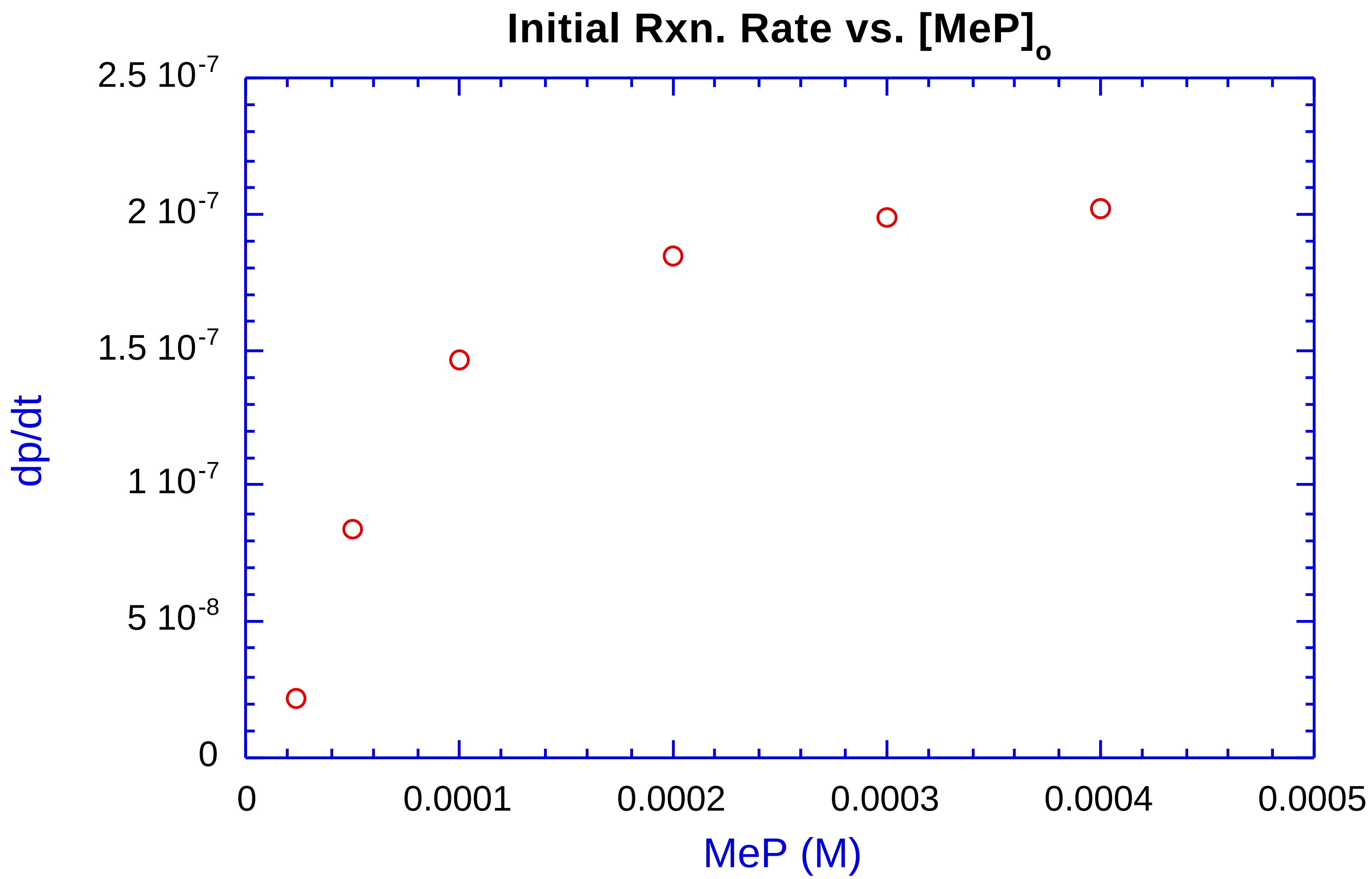
For initial-rate method:

$$\frac{dP}{dt} = \frac{k_{cat} C_{cat} C_A}{K_A + C_A}$$

c.f. M-M equation

$$\frac{dP}{dt} = \frac{k_{cat} C_{cat} C_A}{K_M + C_A}$$

Nitrophenol Production vs. Initial $[MeP]_o$ (Polymer)



Survey of K_m's

Substrate	Catalyst	K_m (M)
NPP	CuL (solution)	1.2×10^{-3}
NPP	CuL (polymer)	8.3×10^{-4}
BNPP	CuL (solution)	2.3×10^{-3}
BNPP	CuL (polymer)	1.0×10^{-4}
MeP	CuL (solution)	7.6×10^{-4}
MeP	CuL (polymer)	5.1×10^{-5}

Comparisons with Other Insoluble Polymers

- **Previous polymers templated with EDA and DETA:**

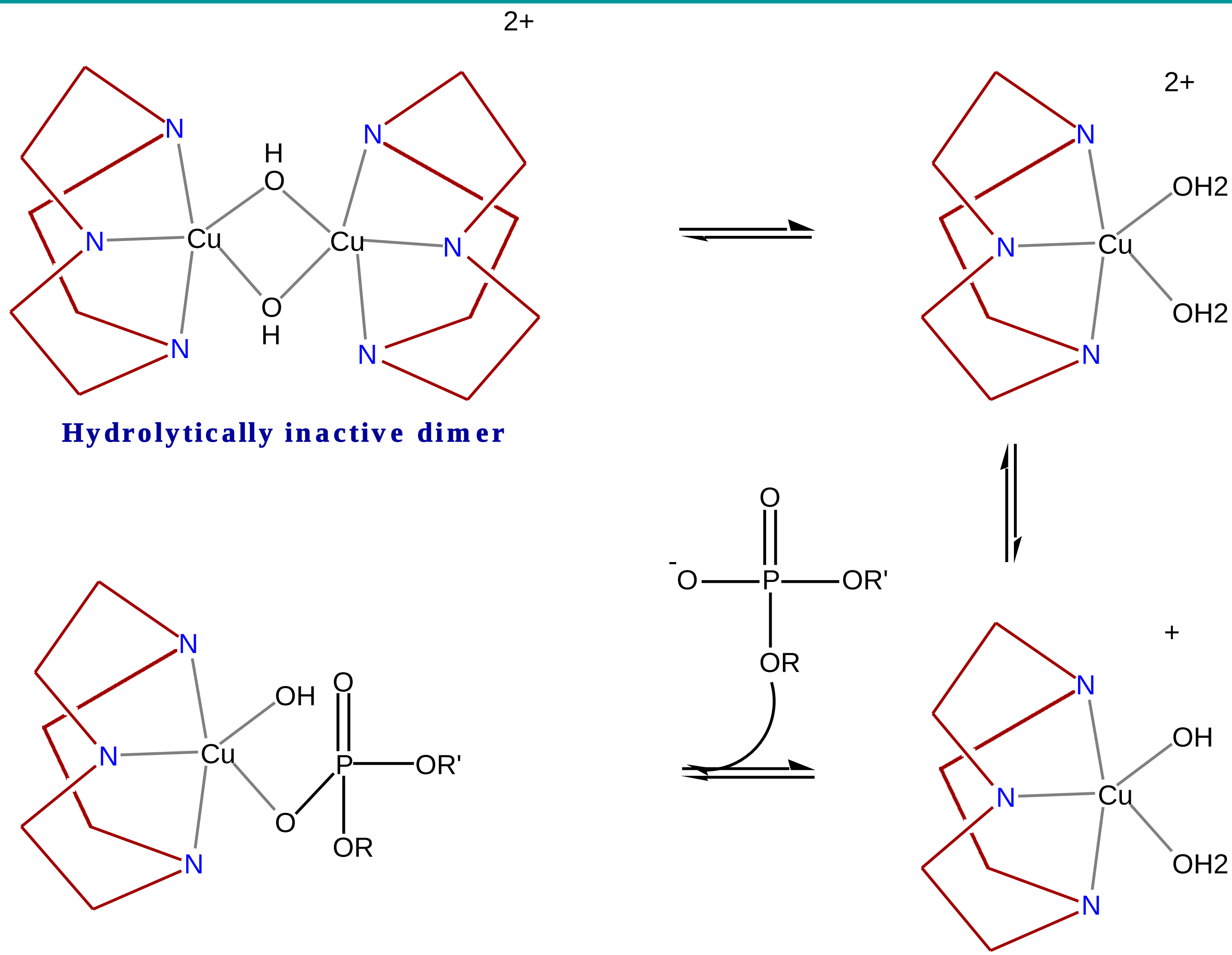
  - NPP rates are similar
  - No reactivity against BNPP

- **Menger and Tsuno* showed 400x enhancement over a phosphate triester (c.f. 6 x 10^5 enhancement)**

- **Srivatsnan and Verma** reported about 600 and 300 fold rate increases for NPP and BNPP using another cross-linked polymer system.**

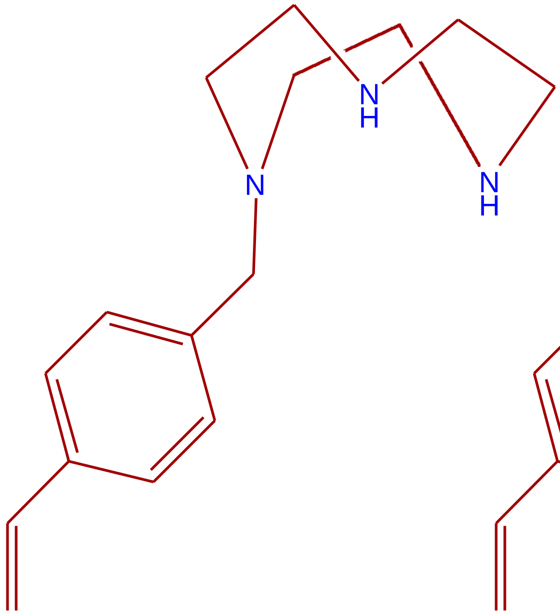
*Menger, F.M., T. Tsuno, J. Am. Chem. Soc. 111, 4903 (1989)
**Srivatsan, S.G. and S. Verma, Chemical Communications, 515-516 (2000).
Srivatsan, S.G. and S. Verma, Chemistry-A European Journal, 7(4) 828-833, (2001).

Another Way to Increase Hydrolysis Rate?



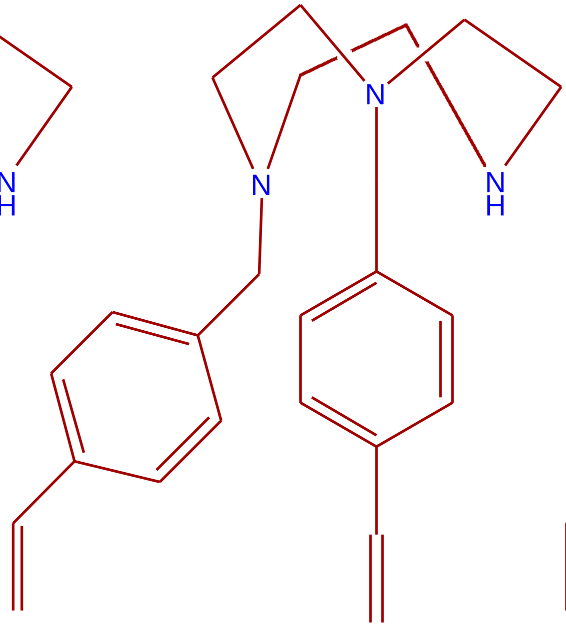
Functionalized Cyclononanes (Polymers)

Polymer 1



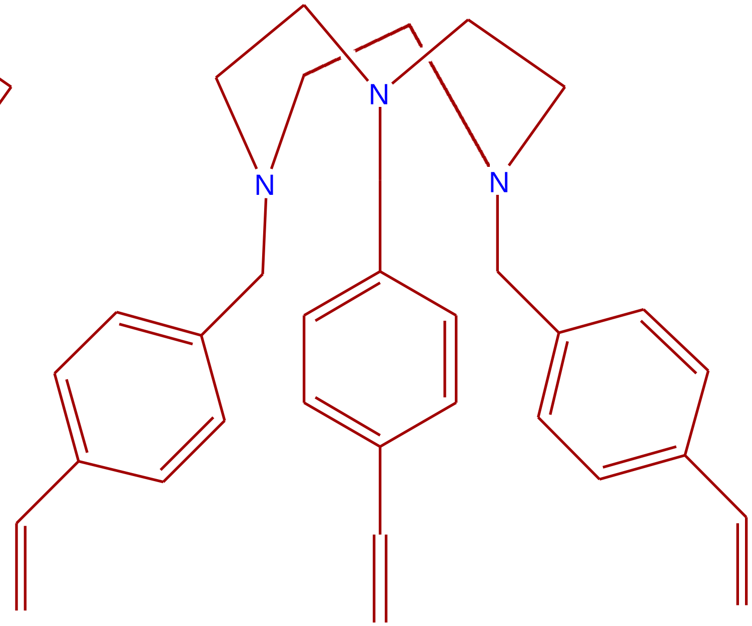
[9]ane(Nvbz)N_2

Polymer 2



[9]ane(Nvbz)$_2$N

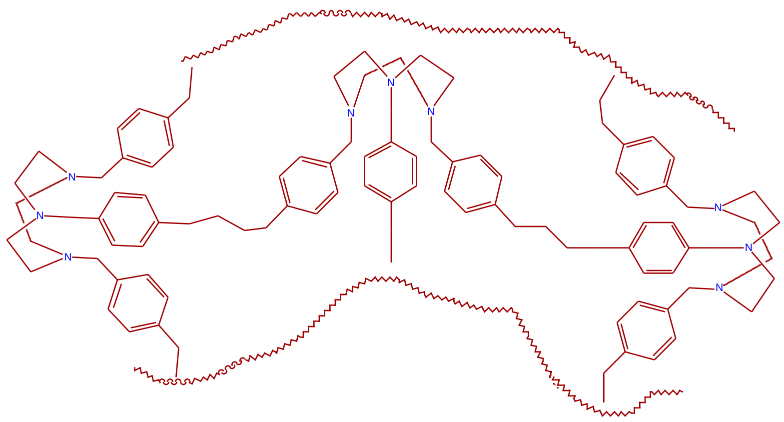
Polymer 3



[9]ane(Nvbz)$_3$

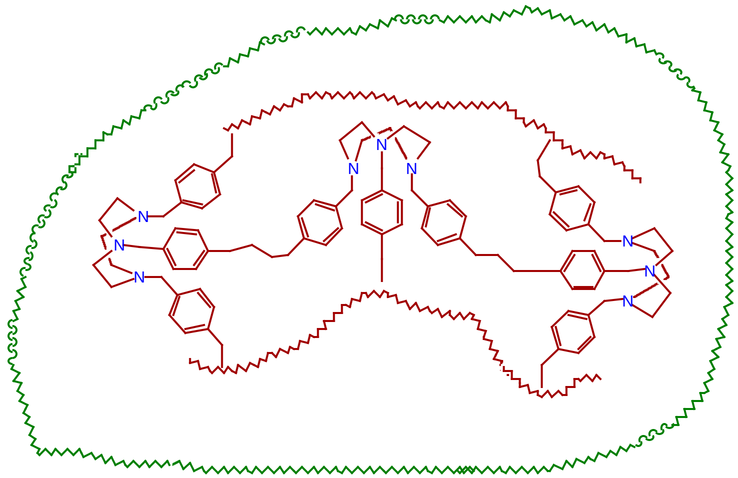
Functionalized Cyclononane Polymers

Polymer 4



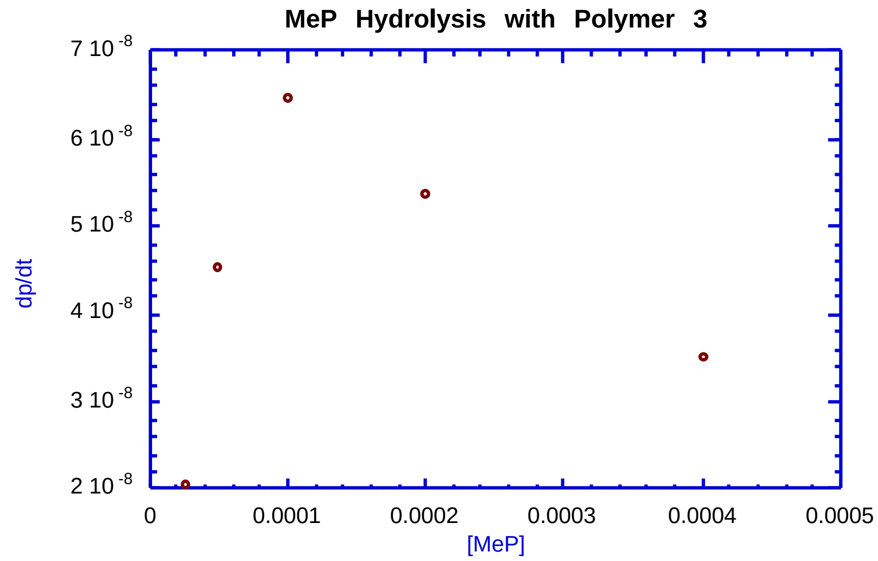
[9]ane(Nvbz)$_3$ polymerized
With AIBN.

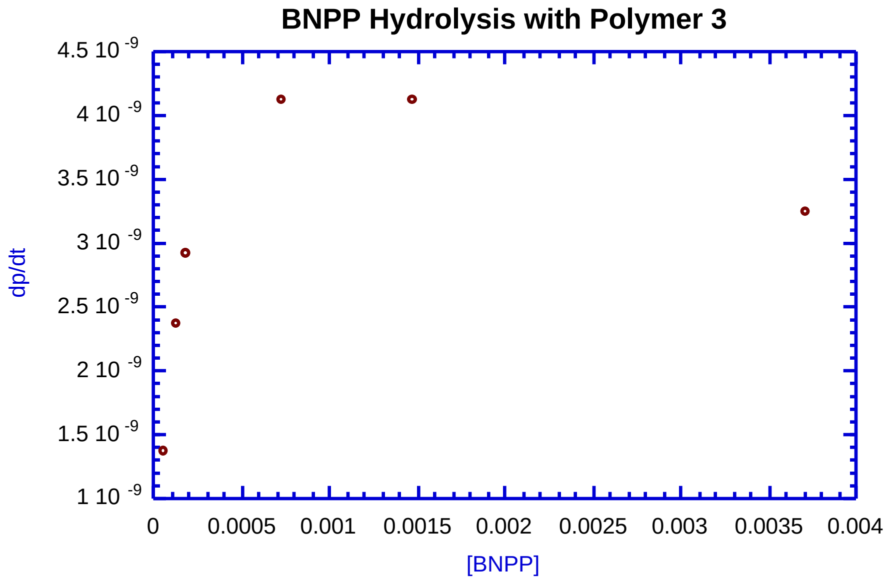
Polymer 5



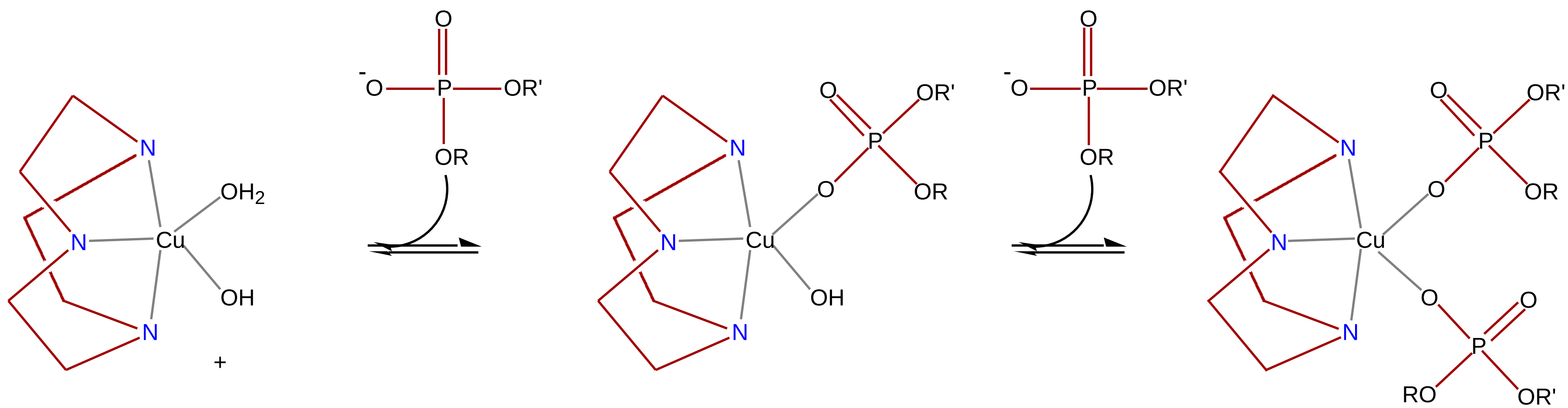
[9]ane(Nvbz)$_3$ polymerized
with added TRIM shell

Polymer (1-3) Kinetics





Inhibition Model

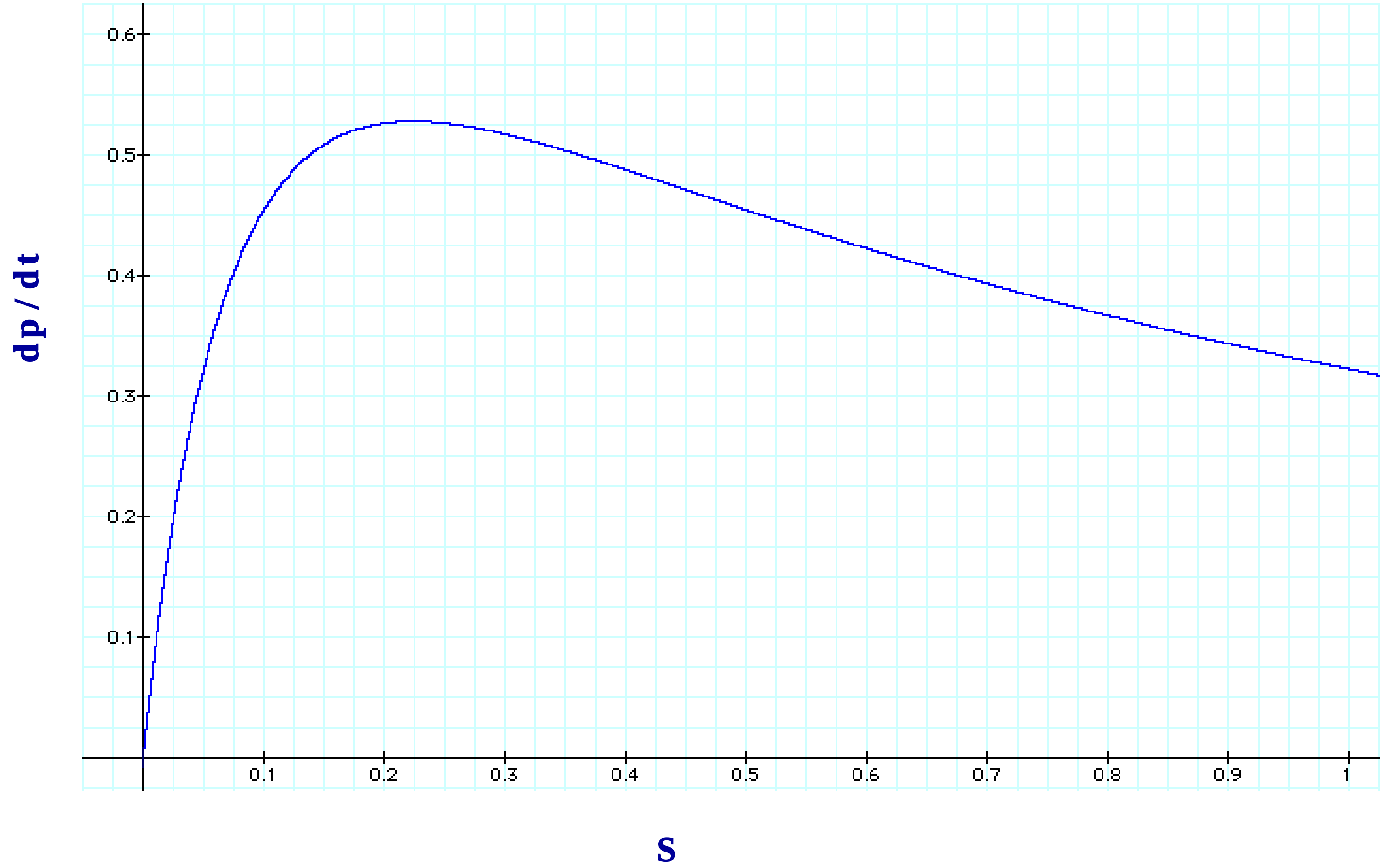


$$
\begin{array}{c}
ES_2 \\
\Big\uparrow\!\!\Big\downarrow \; K \\
C + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} ES \xrightarrow{K_{cat}} C + P
\end{array}
$$

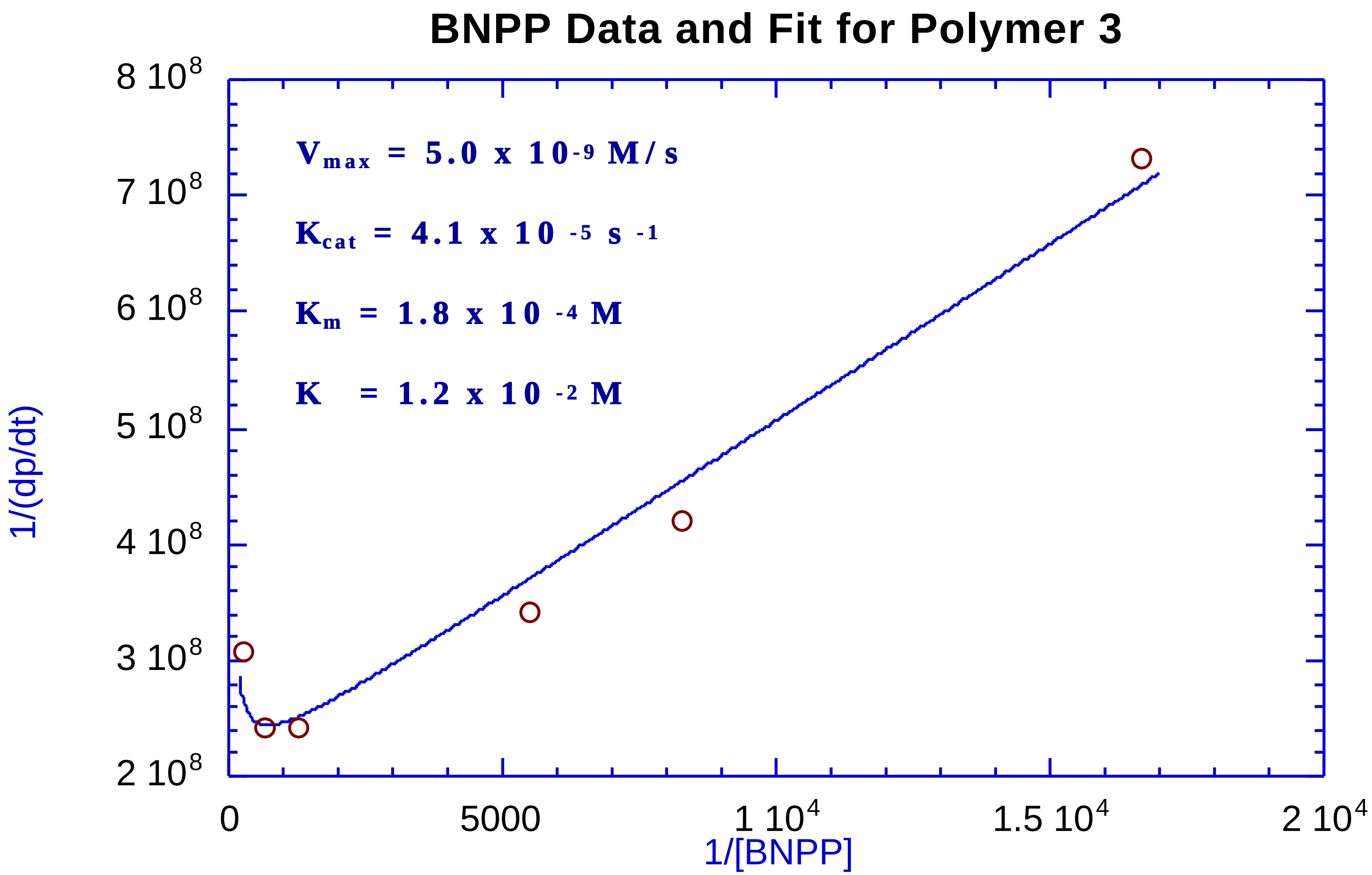
$$
\frac{dp}{dt} = \frac{V_{max}\, s}{K_m + \left(1 + \dfrac{s}{K}\right) s}
$$

Inhibition Model

$$\frac{dp}{dt} = \frac{s}{.1 + (1 + \frac{s}{.5})\,s}$$

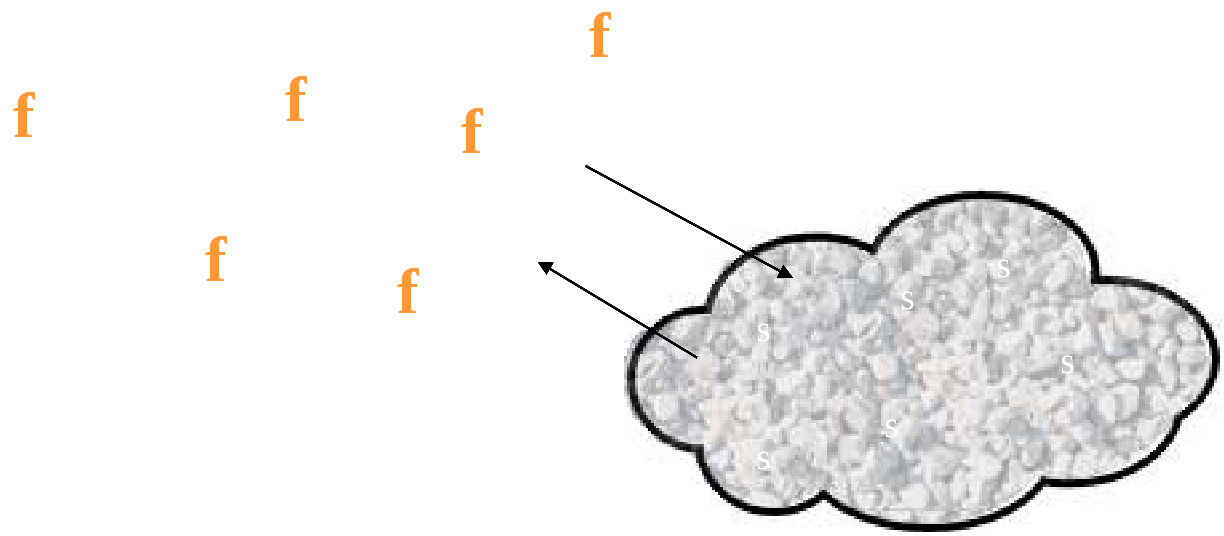


Model Consistent with Data



What's Next?

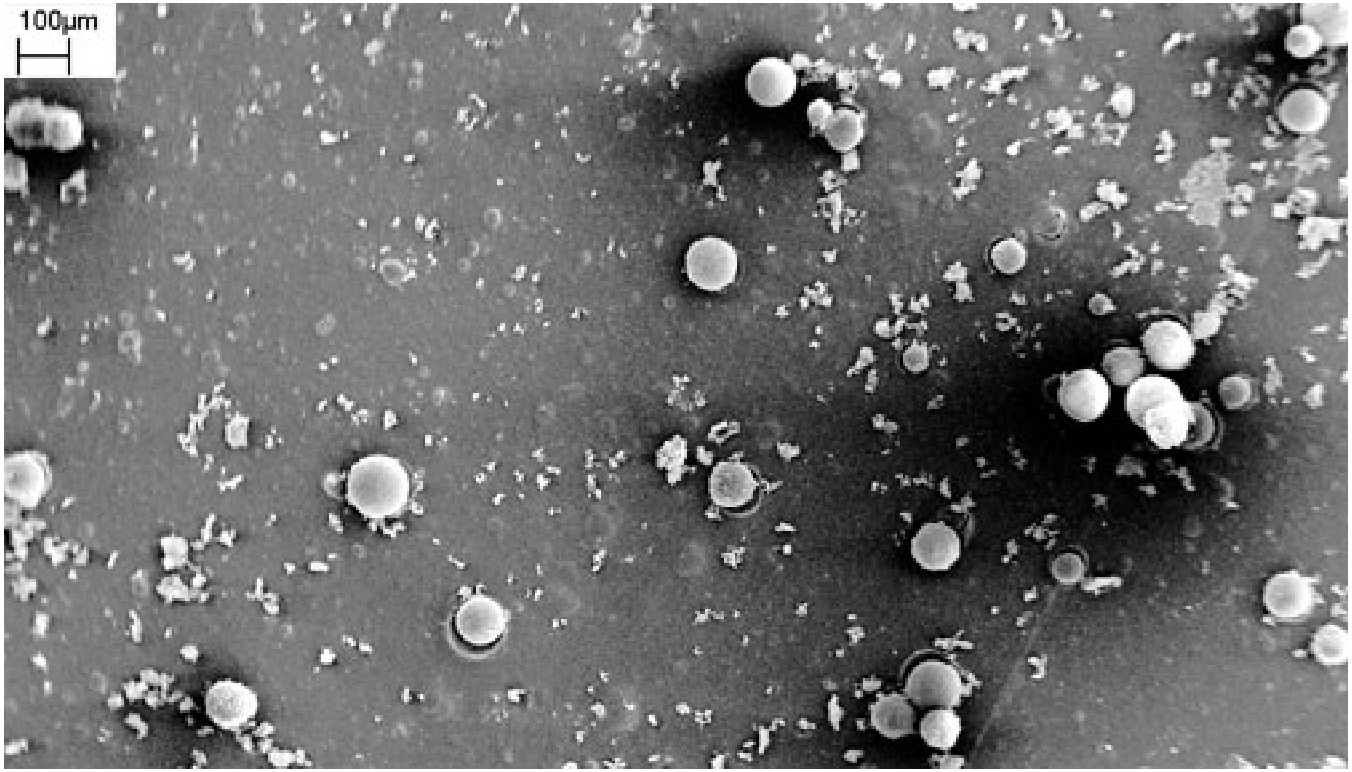
Key to fast hydrolysis is initial concentration of substrate into polymer.



Tune matrix material to attract fluorophosphonates.

What's Next?

Fine powder (400 m^2/g) for foams or ointments.



Tune matrix size/shape for different applications

What's Next?

- Use binunuclear systems to increase rates.

- Investigate non-hydrolytic catalytic systems.

- Apply lessons to making sequence-specific nucleases (6.1).

- Develop for decon kits--either pesticides (AFPMB) or CW agents.

- Incorporate into multilayer, multifunctional coatings or filter membranes (6.2).

Catalysis Summary

- Synthesized several metallopolymers. Polymers have differentiated activities.

- Demonstrated the broad range of target substrates for our metal-chelated catalysts
  - -monoester phosphates
  - -diester phosphates
  - -triester phosphorothionates

- Hydrolysis rates over $6x10^5$ times over uncatalyzed rates.

- Discovered novel property of matrix polymer for strong adsorption of organophosphates.

Publications/Patents

Journal Articles

-Chris M. Hartshorn, Jeffrey R. Deschamps, Alok Singh, and Eddie L. Chang, "Metal-Chelator Polymers as Organophosphate Hydrolysis Catalysts 2: The effects of substituents and polymeric cross-linkers" (review process, 2001)

-Chris M. Hartshorn, Alok Singh, and Eddie L. Chang, "Metal-Chelator Polymers as Organophosphate Hydrolysis Catalysts" (submitted, 2001).

-Q. Lu, A. Singh, J. Deschamps, E. L. Chang, Inorganica Chimica Acta 309, 82-90 (2000).

-R.E. Morris and E. L. Chang, Petroleum Sci. and Tech. 18, 1147-1159 (2000).

-A. Singh, P. Puranik, Y. Guo, and E. L. Chang, Reactive and Functional Polymers 44 79-89 (2000).

Publications/Patents (cont.)

-Dhanajay B. Puranik, Yan Guo, Alok Singh,, Robert E. Morris, A Huang, L. Salvucci, R. Kamin, V. David, and Eddie L. Chang "Copper removal from fuel by solid-supported polyamine chelating agents",, Energy and Fuels 12, 792-797 (1998).

-A. Singh, D. Puranik, Y. Guo, D. Zabetakis, and E. Chang, "Incorporation of metal ion binding sites in polymer matrix by metal ion imprinting", Proc. Matl. Res. Soc. Surface Controlled Nano-Scale Materials for High Value-Added Applications, Vol. 501 pp. 199-208 (1998).

D. Puranik, Y. Guo, A. Singh, R.E. Morris, A. Huang, L Salvucci, R. Kamin, J. Hughes, V. David, and E. Chang, "Removal of copper from fuel by immobilized heterogeneous chelating agents", Proc. 6Th Intl. Conf. Stability and Handling of Liquid Fuels., CONF-971014 , U.S. DOE (Giles, H.N., ed.) 13-30 (1998)

Dhanajay B. Puranik, Vikram A. David, Robert E. Morris, and Eddie L. Chang,"Removal of copper from hydrocarbon fuels using novel azamacrocycle polymers", Energy and Fuels 11(6) 1311-1312 (1997).

Publications/Patents (cont.)

Patents and Disclosures

-"Immobilized metal-chelator complexes for catalysis and decontamination of pesticides and chemical warfare nerve-agents" E. L. Chang, A.N. Singh, Chris M. Hartshorn, and Qin Lu. Combined Navy Case Nos. 79,764 and 82,389 (2001).

-Metal complexing (II)" E.L. Chang, R.E. Morris, and D.B. Puranik, N.C. No. 82,322 (2000).

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